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Profiling of the Oil of the Egyptian Cultivar of Sesame 'Giza 32' Using LC-MS-Based Untargeted Metabolomics †

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Abstract: Sesame (*Sesamum indicum* L.) is an important oil crop whose cultivation is distributed all over the world. Sesame oil has been regarded as functional oil with antioxidant properties in several in vivo studies. In this context, the present study describes the metabolic profiling of the oil extracted from sesame seeds to provide new clues about the composition of minor components, including phenolic compounds. It was performed using reversed-phase high-performance liquid chromatography coupled with diode array detection, and quadrupole-time-of-flight-mass spectrometry (MS), and tandem MS/MS. The characterization of the metabolites was based on their retention time, UV spectra, accurate MS, and MS/MS data. In this way, 86 compounds were characterized and belonged to several classes, namely, phenolic acids, flavonoids, lignans, organic acids, and amino acids. Among them, 64 metabolites seem to pass directly from the cake to the oil and hence contributing to its antioxidant potential. Further studies are needed to figure out the presence of such phenolics in virgin oil and after oil refining and the influence in its functionality since most studies only characterized lignans like sesamol.

Keywords: sesame oil; *Sesamum indicum* L.; RP-HPLC-DAD-QTOF-MS; seed oil; phenolic acids; flavonoids; lignans

1. Introduction

Sesame (*Sesamum indicum* L.) is an oil crop whose cultivation is distributed all over the world. Its production is nearly 7 million tons [1]. Anciently, sesame was originated from India. It was known in the Ancient Egyptian Civilization for the treatment of asthma since the third century BC., Sesame seeds represent a rich source of fats, dietary fibers, carbohydrates, vitamins, and proteins [2,3]. The

content of fat is around 50% [3] and so it is one of the main use of sesame, with a global production of 2 million tons of sesame oil [1].

A myriad of studies unraveled the biological potentials and phytochemicals of sesame. In this context, Dravie et al. [4] performed multiple solvent extractions for sesame seeds cultivated in Ghana with a focus on their antioxidant potentials and total phenol and flavonoids contents. The total phenol content of the extracts was positively correlated with the antioxidant potential. As a matter of fact, sesame seeds possess different biological potentials as hypolipidemic, hypocholesterolemic, antidiabetic, anticancer, antioxidant, antihypertensive, antileishmanial activity, and cardioprotective potentials [3,5,6]. Similarly, seed oil has been recently regarded as functional oil with antioxidant properties [7,8] and auditory-protective effects [9], among others.

With regard to agri-food residues produced from sesame, Mekky et al. [10] unraveled the phytochemical composition of sesame cake carrying out untargeted metabolic profiling via reversed-phase (RP) high-performance liquid chromatography (HPLC) coupled to diode array detection (DAD) and quadrupole-time-of-flight (QTOF)-mass spectrometry (MS) based method. Lignans, flavonoids, and phenolic acids were the main phenolic classes in the cake of this cultivar and hence providing an insight into this agri-food residue significance. Following this strategy, the objective of this study was to carry out an untargeted metabolic profiling of sesame oil to give new clues about the composition of its minor components, including phenolic compounds, which can provide antioxidant potential and functionality to the oil. Moreover, as in other oils, the phenolic composition is related to their initial content in the closer tissues [11], the phenolic composition of the sesame oil was compared to the cake counterpart.

2. Materials and Methods

Sesame seeds from the Egyptian cultivar Giza 32 (SG32) were treated as in Figure 1 to recover the oil fraction and the cake. Then, the extraction of phenolics from SG32 was according to Shyu et al. [12] using methanol:water (80:20, *v*/*v*). The extract was further subjected to RP-HPLC–DAD–QTOF-MS and -MS/MS according to Mekky et al. [10], using electrospray in the negative ionization mode.

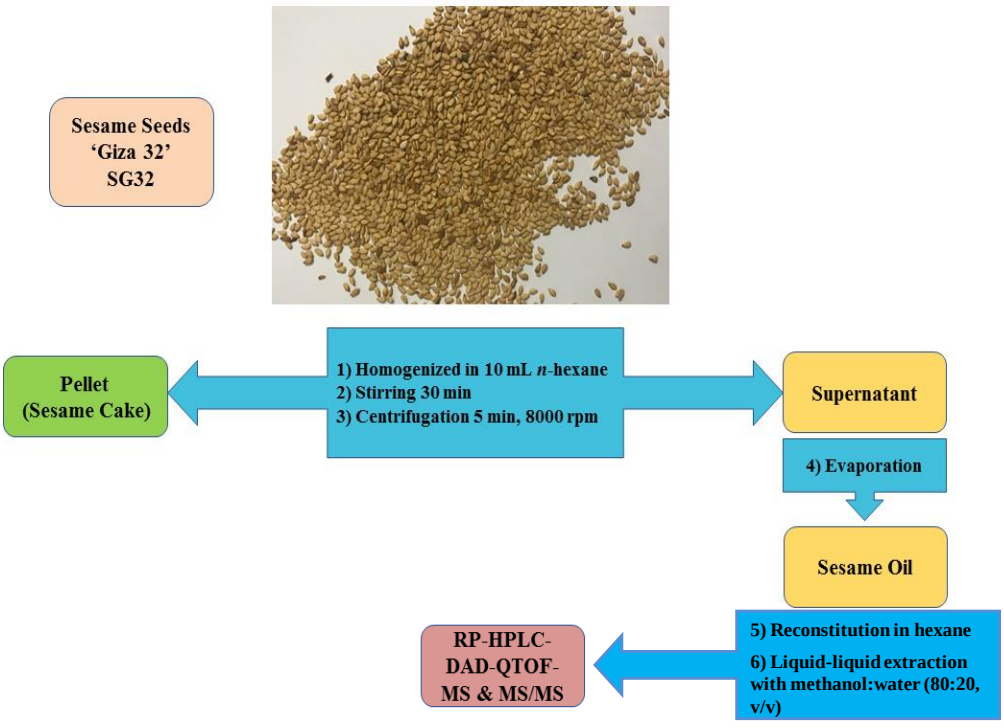

Figure 1. Scheme followed to recover sesame oil and extract phenolic compounds.

3. Results and Discussion

3.1. RP-HPLC-DAD-QTOF-MS and MS/MS Characterization

The compounds were characterized according to the retention time, experimental *m*/z, generated molecular formulae, mass error (ppm), mass score, double bond equivalents (DBE), UV maxima, tandem mass fragments, and relative abundance [10,13–15]. A total of 86 compounds were found and classified into phenolics (64) and non-phenolic compounds (22). Table 1 illustrates the number of compounds found and the relative abundance of each metabolite.

Table 1. Classification, number of compounds found per class, and relative in sesame oil.

Class	Number	Mean Area
Phenolic metabolites		
Coumarins	1	1.60×10^4
Flavonoids	19	1.48×10^7
Hydroxybenzoic acids	13	7.54×10^6
Hydroxycinnamic acids	19	9.47×10^6
Lignans	10	1.20×10^7
Phenol derivatives	1	1.43×10^5
Phenolic aldehydes	1	1.14×10^5
Non-phenolic metabolites		
Amino acids	8	9.82×10^6
Peptides	1	1.25×10^6
Organic acids	13	2.28×10^7

Lowest value Highest value

As an example of the characterization work, Figure 2a,b show the fragmentation pattern of vanillic acid (*m*/*z* 167.03) and verbascoside (*m*/*z* 623.20) as an example hydroxybenzoic and hydroxycinnamic acids. In these fragmentation patterns, the presence of the neutral loss of CO_2 (44 Da) was observed from vanillic acid and the caffeic acid moiety that forms part of verbascoside, which is common in both phenolic types. Additionally, the neutral loss of a methyl moiety was also observed in the case of the former compound, while verbascoside spectrum showed the loss of hexosyl and deoxyhexosyl moieties which is characteristic of *O*-glycosylated compounds [10,14]. Their UV spectrum agreed well with the literature with maxima at 258 nm and 275 nm, respectively [10,16].

Moreover, Figure 3a,b show examples of the fragmentation pattern of flavonoids and lignans, i.e., quercetin 3-*O*-β-D-glucopyranoside (*m*/*z* 463.09) and hydroxysesamolin trihexoside (*m*/*z* 871.25). The UV absorbance of the former compound showed two maxima at around 250 nm and 352 nm suggesting a flavonol nucleus. Moreover, its MS/MS spectra showed the neutral loss of a hexosyl moiety (162 Da), unraveling the presence of an aglycone with *m*/*z* value of 301, and the occurrence of other fragments at *m*/*z* 179.00 ($^{1,2}A^-$) and 151.00 ($^{1,3}A^-$) produced through the retro Diels–Alder fission and retro-cyclization [10].

In the case of lignans, the aglycone part was furofuran type and they appeared as conjugates with hexosyl moieties. In Figure 3b the neutral loss of three hexosyl moieties is observed along with the presence of the aglycone of *m*/*z* 385.09. The fragmentation of the aglycone revealed ions at *m*/*z* 179.06 and 137.03 after the cleavage of the tetrahydrofuran ring [10]. Thus, this novel compound found in sesame oil was described as hydroxysesamolin trihexoside.

In a similar way, i.e., studying the information provided by RP-HPLC-DAD-MS and -MS/MS, databases, and literature, the rest of the compounds were characterized.

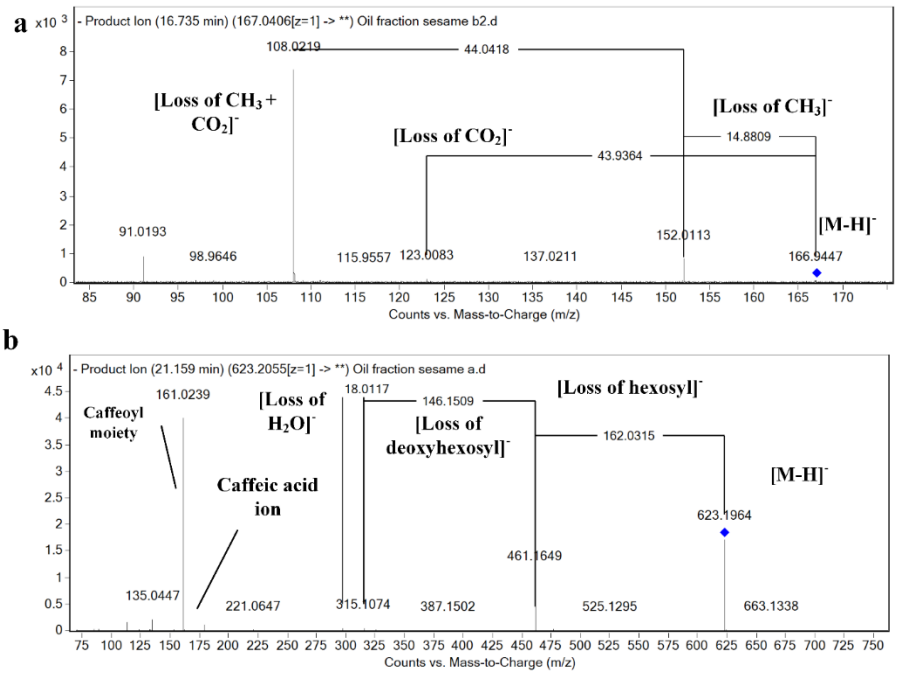

Figure 2. Fragmentation patterns of (**a**) vanillic acid, (**b**) verbascoside.

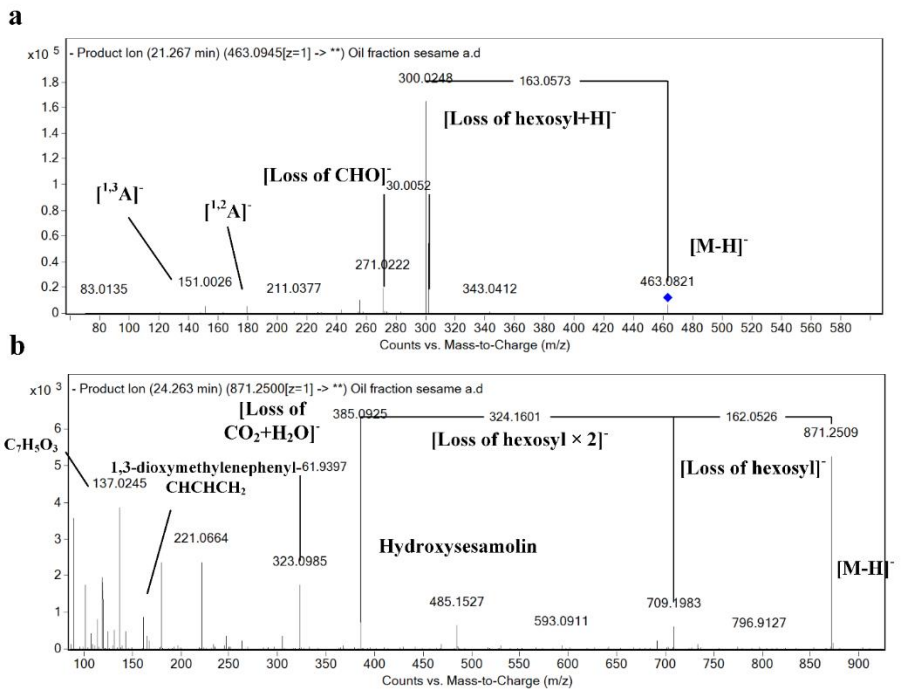

Figure 3. Fragmentation patterns of (**a**) quercetin 3-*O*-β-D-glucopyranoside, (**b**) hydroxysesamolin trihexoside.

3.2. Comparison between Sesame Oil and Cake

The presence of 112 metabolites belonging to the aforementioned classes in SG32 oil were found in the cake counterpart [10]. From these compounds, 64 metabolites were observed in both SG32 cake and oil (Figure 4). These compounds were mainly from all the aforementioned classes. The other 22 belonged to phenolics, with the presence of phenol aldehydes, and amino acids and the absence of sugars.

As a matter of fact, phenolic compounds could contribute to the biological importance of the oil, as the cake extracts have shown antioxidant properties [10]. In another perspective, further study will

be performed in virgin sesame oil obtained by pressing and refined sesame oil since the industrial oil processes could contribute to the loss or change in the content of these biologically important metabolites, including lignans derivatives [17,18].

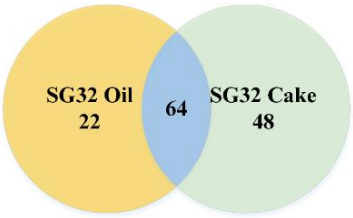

Figure 4. A Venn diagram illustrating the common metabolites between SG32 oil and SG32 cake.

4. Conclusions

The present study demonstrates the first report dealing with the metabolic profiling of sesame oil using RP-HPLC–DAD–ESI–QTOF-MS and -MS/MS. It provided information about that the oil contains 86 metabolites, mainly belonging to the phenolic class. Among them, 64 metabolites were commonly present in both SG32 oil and cake. Further studies are required to trace the presence of biologically important metabolites in commercial sesame oils.

Authors Contributions: Investigation, R.H.M. and M.d.M.C.; Methodology, M.d.M.C.; Data analysis, R.H.M.; Validation, R.H.M., M.d.M.C.; Writing—Original Draft, R.H.M.; Writing—Review & Editing; M.d.M.C., E.A.-S., and A.S.-C.; Supervision, E.A.-S., A.S.-C., and M.d.M.C. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest: The authors declare no conflict of interest.

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